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OUTGASSING OF SHIPBOARD HYDRAULIC FLUIDS.(U)

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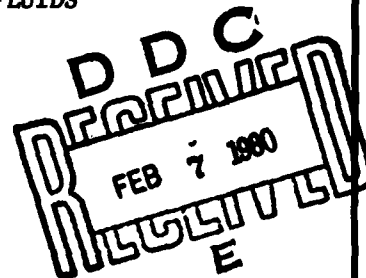
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OUTGASSING OF SHIPBOARD HYDRAULIC FLUIDS

By

Peter Demas



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OUTGASSING OF SHIPBOARD HYDRAULIC FLUIDS

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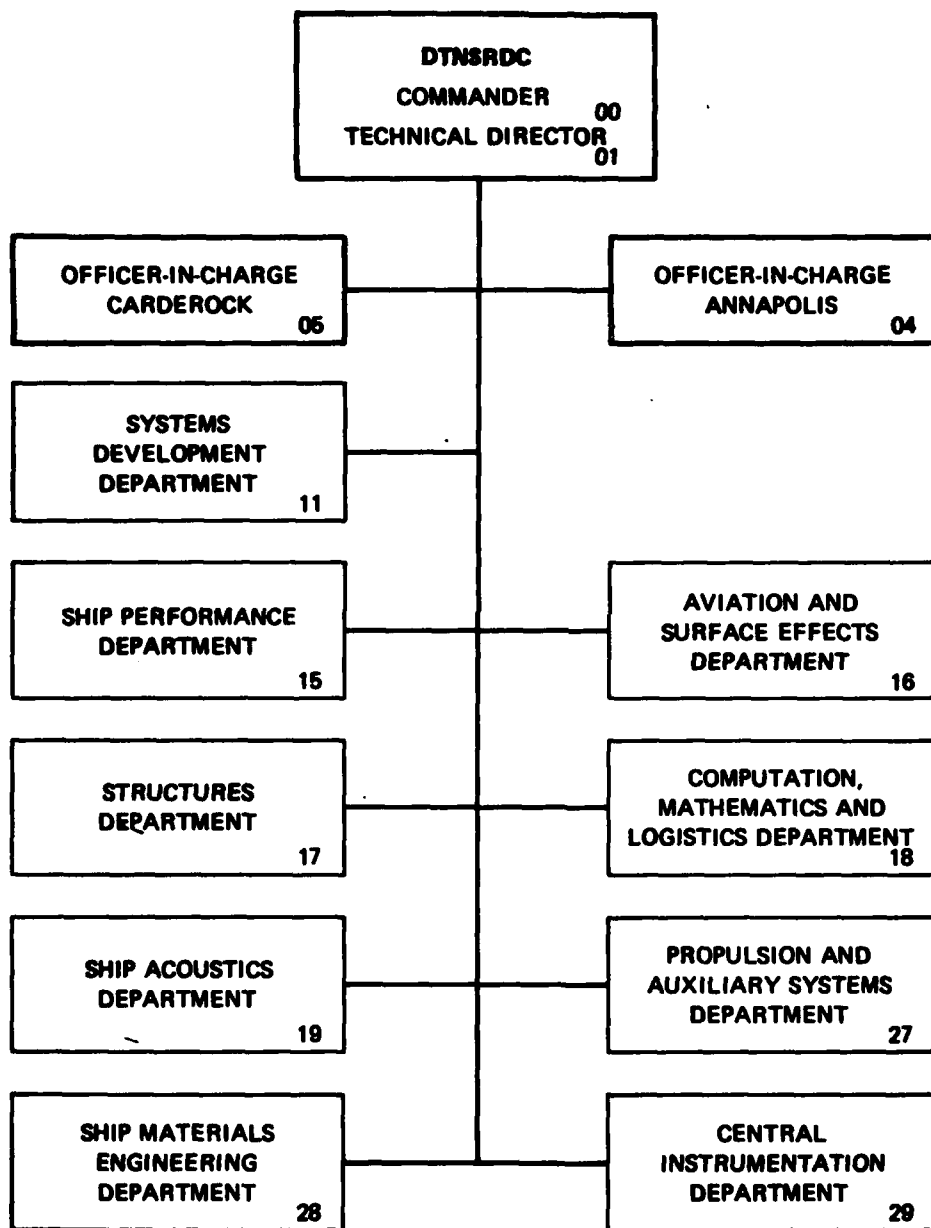
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↘ The samples were sequentially exposed to temperatures of 50<sup>o</sup>, 100<sup>o</sup>, 250<sup>o</sup>, and 450<sup>o</sup> C each for 3 hours, and the types and amounts of the outgassed products were determined.

The neopentyl polyol ester hydraulic fluid emitted large amounts of carbon monoxide, aldehydes, and nitrogen oxides at 250<sup>o</sup> and above. The triaryl phosphate hydraulic fluid emitted amounts of carbon monoxide, nitrogen oxides, and aldehydes in excess of the threshold limit value only when heated to 450<sup>o</sup> C. It contained a large amount of a phenol-type constituent. The petroleum base hydrocarbon hydraulic fluid emitted carbon monoxide at 250<sup>o</sup> C and above and aldehydes at 450<sup>o</sup> C in excess of threshold limit values. Of these emissions, the carbon monoxide and aldehydes from the neopentyl polyol ester and the phenol-type constituent from the triaryl phosphate are the most potentially hazardous.

It is recommended that further outgassing studies be carried out on additional samples of each of the classes of hydraulic fluids studied to establish whether or not the behavior observed in this study is typical. This will provide a basis for materials modifications/substitutions to reduce potential hazards. ↗

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## TABLE OF CONTENTS

	Page
LIST OF FIGURES . . . . .	111
LIST OF TABLES . . . . .	111
LIST OF ABBREVIATIONS . . . . .	iv
ABSTRACT . . . . .	1
ADMINISTRATIVE INFORMATION . . . . .	1
INTRODUCTION . . . . .	2
MATERIALS . . . . .	3
EXPERIMENTAL PROCEDURES . . . . .	3
FLUID CHARACTERIZATION PROCEDURES . . . . .	3
OUTGASSING PROCEDURES . . . . .	4
RESULTS AND DISCUSSION . . . . .	6
FLUID CHARACTERIZATION . . . . .	6
OUTGASSING STUDIES . . . . .	8
CONCLUSIONS . . . . .	12
RECOMMENDATION . . . . .	12
APPENDIX - METHOD FOR PHOSPHINE DETERMINATION . . . . .	17
REFERENCES . . . . .	19

### LIST OF FIGURES

1 - Apparatus for Heat Exposure and Collection of Outgassed Products of Hydraulic Fluids . . . . .	13
2 - Gas Chromatogram of Neopentyl Polyol Ester . . . . .	14
3 - Gas Chromatogram of Triaryl Phosphate . . . . .	15
4 - Gas Chromatogram of Petroleum Base Hydrocarbons . . . . .	16

### LIST OF TABLES

1 - Constituents of Vapor Outgassed from Neopentyl Polyol Ester Hydraulic Fluid (0.0460 Gram-Sample) . . . . .	9
2 - Constituents of Vapor Outgassed from Triaryl Phosphate Hydraulic Fluid (0.0540 Gram-Sample) . . . . .	10
3 - Constituents of Vapor Outgassed from Petroleum Base Hydrocarbons Hydraulic Fluid (0.0458 Gram-Sample) . . . . .	11

# LIST OF ABBREVIATIONS

$\text{CS}_2$	Carbon disulfide
CO	Carbon monoxide
$^{\circ}\text{C}$	Degree Celsius
e.g.	For example
$\text{ft}^3$	Cubic feet
g/kg	Gram per kilogram
g/l	Gram per liter
kg	Kilogram
$\mu\text{g}$	Microgram
ml	Milliliter
ml/min	Milliliter per minute
mm	Millimeter
MBTH	3-methyl-2-benzothiazolinone hydrazone hydrochloride
$\text{m}^3$	Cubic meter
ppm	Part per million
ppm/kg	Part per million per kilogram
TLV	Threshold limit value (American Conference of Governmental Industrial Hygienist, 1979)
$\text{NO}_x$	Nitrogen oxides
HCHO	Formaldehyde
FID	Flame ionization detector
GC	Gas chromatograph
GC/MS	Gas chromatograph/mass spectrometer
MS	Mass spectrometer
$\text{AgNO}_3$	Silver nitrate
HCl	Hydrochloric acid
$(\text{NH}_4)_6\text{MoO}_{24} \cdot 4\text{H}_2\text{O}$	Ammonium molybdate
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	Stannous chloride
$\text{PO}_4^{3-}$	Phosphate
$\text{PH}_3$	Phosphine
%	Per cent
N	Normality

### ABSTRACT

The outgassing characteristics of single samples of three classes of Navy hydraulic fluids were investigated in order to help establish a basis for determining the potential toxicity of resulting gases in ships' atmospheres. Hydraulic fluids studied were:

1. Neopentyl polyol ester (MIL-L-23699B)
2. Triaryl phosphate (experimental)
3. Petroleum base hydrocarbons (MIL-L-17331F)

The samples were sequentially exposed to temperatures of 50°, 100°, 250°, and 450° C each for 3 hours, and the types and amounts of the outgassed products were determined.

The neopentyl polyol ester hydraulic fluid emitted large amounts of carbon monoxide, aldehydes, and nitrogen oxides at 250° and above. The triaryl phosphate hydraulic fluid emitted amounts of carbon monoxide, nitrogen oxides, and aldehydes in excess of the threshold limit value only when heated to 450° C. It contained a large amount of a phenol-type constituent. The petroleum base hydrocarbon hydraulic fluid emitted carbon monoxide at 250° C and above and aldehydes at 450° C in excess of threshold limit values. Of these emissions, the carbon monoxide and aldehydes from the neopentyl polyol ester and the phenol-type constituent from the triaryl phosphate are the most potentially hazardous.

It is recommended that further outgassing studies be carried out on additional samples of each of the classes of hydraulic fluids studied to establish whether or not the behavior observed in this study is typical. This will provide a basis for materials modifications/substitutions to reduce potential hazards.

### ADMINISTRATIVE INFORMATION

This report is part of the David W. Taylor Naval Ship Research and Development Center's program to investigate potentially hazardous outgassing from shipboard materials under Program Element 62543N, Task Area ZF 43451001, Work Unit 2831-162. The work is sponsored by Naval Material Command, NAVMAT 08T23 (T. Hinton), through the Naval Research Laboratory (Code 6180 (Dr. H. Carhart)).



## INTRODUCTION

Outgassing due to heating of organic materials used in ships and submarines is one of the major contributors of potentially hazardous contaminants in breathing atmospheres. Since knowledge and control of outgassing characteristics of organic materials is important to the safety of the crew, this Center has been investigating emissions from organic materials exposed to elevated temperatures below flame conditions in the presence of large volumes of air. These conditions are considered characteristic of situations that would be encountered aboard ship, e.g.,\* a protective coating near or in contact with a hot steam pipe or electrical system. Gaseous emissions include volatilized components, thermal degradation products, and absorbed gasses and liquids.

New ship materials are constantly sought and developed. They may be placed in service with emphasis on their superior performance without proper consideration of their outgassing characteristics. Materials investigated at this Center have included:

1. Paints and adhesives.
2. Thermal and electrical insulations.
3. Fire-retardant materials.
4. High temperature resistant materials.

This report documents an outgassing study of three liquid hydraulic fluids: neopentyl polyol ester, triaryl phosphate, and petroleum base hydrocarbons.

Outgassing studies of solid materials such as those studied previously, do not present serious obstacles since outgassing is easily controlled with respect to temperature. However, liquids, such as the hydraulic fluids of the current study, tend to distill. Due to this distillation, they cannot be subjected to temperatures higher than the boiling points of their constituents unless confined in a closed system. Consequently, this report also describes techniques used to characterize outgassing from liquids and analyze their emissions.

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\*Definitions of abbreviations may be found on page iv.

## MATERIALS

The three hydraulic fluids investigated are described below. One member of each class was studied. Some general information is also presented on their service applications.

1. Neopentyl polyol ester hydraulic fluids meet the requirements of MIL-L-23699B.<sup>1\*</sup> This type of hydraulic fluid is used in surface effect vehicles both as a hydraulic fluid and as a gas turbine oil. It is also used in DD963 class ships as a gas turbine lubricant. The sample studied was a dark, amber-colored liquid.

2. Triaryl phosphate hydraulic fluids meet MIL-H-19457B (SHIPS).<sup>2</sup> These are fire resistant fluids used in deck-edge weapon elevators on aircraft carriers. In this investigation an experimental dark amber-colored synthetic triaryl phosphate was studied.

3. Petroleum base hydrocarbons meet the requirements of MIL-L-17331F.<sup>3</sup> They are used on all submarines and surface ships, representing the largest single category of oils used on Navy ships. It is the primary oil for steam turbine lubrication and is also used in ship hydraulic systems when a fire resistant hydraulic fluid is not required. The sample studied was a light, amber-colored liquid.

## EXPERIMENTAL PROCEDURES

### FLUID CHARACTERIZATION PROCEDURES

To provide an insight into their natures and characteristics, and thereby to provide guidance for the outgassing studies, the three hydraulic fluids were subjected to three tests. The first test was GC/MS examination.\*\* The GC was a VARIAN<sup>TM</sup> Model 3760 gas chromatograph with a (5%) SP 2100\*\*\* packed stainless steel column (1/8-inch outside diameter x 12 feet long), interfaced to the mass spectrometer with a Biemann-Watson separator.

\*A complete listing of references appears on page 19.

\*\*Conducted at Georgetown University, Washington, D. C., under the supervision of Professor C. Hammer, Department of Chemistry.

\*\*\*Supelco Incorporated, Supelco Park, Bellefonte, PA.

SP 2100 is a methylsilicone type column packing material resistant to 350° C. The GC was temperature programmed from 250° to 310° C. The MS was an Associate Electronics Industries Model 1201.

In the second test, incipient boiling points were determined with a Gallenkamp apparatus (a boiling point-melting point apparatus of British manufacture) using capillary tubes, in air, and observing the first air bubble with a magnifying lens.

In the third test, one microliter of a 0.01% solution of each hydraulic fluid in CS<sub>2</sub> was injected into a Hewlett-Packard Model 5750 gas chromatograph employing a 1/8-inch outside diameter, 12-foot-long stainless steel column packed with 5% SP 2100. The unit was programmed at a 4° C/min temperature rise rate from 120° to 300° C. Helium was used as the carrier gas and a FID was employed.

#### OUTGASSING PROCEDURES

Several techniques for studying outgassing of liquids were evaluated before settling on a suitable technique. Three methods found unsuitable were:

1. The head space vapors generated at ambient temperatures were examined by GC, but the low volatility of the fluids resulted in an absence of GC peaks.
2. A Hewlett-Packard Model 18580A Pyroprobe\* was attached to the GC but the resultant chromatograms, obtained at various temperatures, did not yield reproducible results with the undiluted fluids.
3. An aliquot portion of fluid in a platinum boat was sealed in a glass container and heated to various selected temperatures in an oven; the resultant vapors were examined by GC techniques. After some experimentation to correct deficiencies, this last procedure was judged unsatisfactory because condensation of the sample on the glass walls near the platinum boat caused inconsistent results and also because the procedure represented a static condition rather than a dynamic one as it is prevalent in shipboard environment.

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\*An apparatus that enables viscous and solid samples to be introduced into a gas chromatograph instantaneously evaporating them into the column and thus chromatograms of such materials can be obtained.

The method finally chosen utilized an apparatus that had been previously designed and constructed by the Center for outgassing studies of solid materials. This apparatus was adapted for handling liquid samples (see Figure 1). The experimental system consists of a heat exposure and pyrolysis chamber (P) made from a Pyrex tube 10-mm inside diameter, 150-mm long surrounded by a heating electric coil (U), and wrapped up with a glass tape to prevent heat loss. A platinum boat (S) contains the liquid sample. Two gas-scrubbing impingers ( $I_1, I_2$ ) each containing 10-ml of distilled water, trap water-soluble constituents present in the outgassed products. Calcium chloride tube (D) absorbs moisture. Two activated charcoal tubes ( $C_1, C_2$ ) in series absorb any gaseous organic constituents not retained by the impingers. A flowmeter (F) indicates the flow circulation rate (normally 50 ml/min), generated by an air circulating pump (E). A removable Swage-lock<sup>TM</sup> fitting (W) permits the introduction of the platinum boat containing the sample into the heat exposure chamber. Port (U) permits withdrawal of gaseous samples from the assembly. Thermocouple (T), connected to a potentiometer, monitors the temperature.

The procedure used to generate outgassed products started with weighing an aliquot portion of hydraulic fluid into the platinum boat which was then inserted into the heat exposure chamber. The chamber was sealed. With the impingers, drying tube, and charcoal tubes in place, the circulating air pump and heat were turned on. The sample was exposed stepwise, for 3-hour periods to temperatures of 50°, 100°, 250°, and 450° C. The volatile constituents from each exposure, if any, were absorbed by the scrubbing impingers and the activated charcoal tubes as they were swept out of the heating chamber by the circulating air. Impinger solutions and activated charcoal tubes were removed for analysis at the end of each 3-hour exposure period and replaced with new ones for the following higher temperature exposure period. The assembly was purged with clean air but the remainder of the sample was left in the platinum boat for the next higher temperature exposure period.

The solutions produced in the impingers during each 3-hour period were handled separately and analyzed for nitrogen oxides ( $NO_x$ ),\* aldehydes

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\*Reported as a group since funds and time did not permit identification of individual compounds.

(expressed as HCHO),\* total volatile phosphorus (as phosphine),\* and total hydrocarbons.\* The NO<sub>x</sub> contents were determined by the Saltzman procedure<sup>4</sup> by reacting a measured volume of impinger solution with sulfamic acid and spectrophotometrically measuring the light absorbance of the resulting solution at 550 nanometers. The aldehyde content was determined by the MBTH method<sup>5</sup> by reacting MBTH with a measured volume of impinger solution and measuring the absorbance of the resulting colored solution at 628 nanometers. The total phosphorus content was determined by a method, described in the appendix, developed specifically for these outgassing studies since no method suitable for the determination of total volatile phosphorus was available in the literature. The hydrocarbon contents were determined by GC.

Hydrocarbons not retained in the impingers were adsorbed by the charcoal tubes. The charcoal tubes were analyzed for total adsorbed hydrocarbons (expressed as methane) by extraction with CS<sub>2</sub><sup>6</sup> followed by injecting an aliquot portion of the resultant CS<sub>2</sub> solution into a Hewlett-Packard 5730A gas chromatograph using a 1/8-inch outside diameter x 12-foot-long stainless steel column packed with (5%) SP 2100. The carrier gas was helium at 32 ml/min and the GC was programmed for 4° C/min temperature rise from 120° to 310° C.

The air circulating in the heat exposure apparatus was sampled by a syringe through Port J of the heat exposure apparatus two or three times during each 3-hour temperature step. These samples were analyzed for CO by a method in which the CO is converted catalytically to methane which is then measured by GC using an FID.<sup>7</sup>

## RESULTS AND DISCUSSION

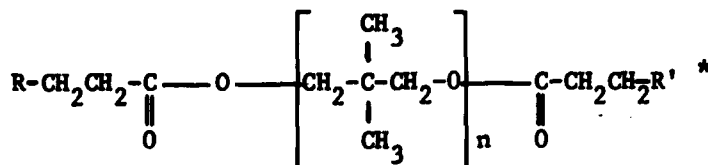
### FLUID CHARACTERIZATION

#### GC/MS Examinations

The neopentyl polyol ester hydraulic fluid was found to be a mixture of several polymeric esters of 1,3-dihydroxynepentane. Based on the mass spectra obtained, it probably has the following structure:

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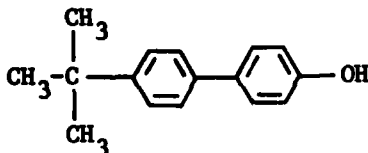
\*Reported as a group since funds and time did not permit identification of individual compounds.



\*R, R' may be straight or branched aliphatic chains of indeterminate length.

It was also observed that the sample begins to boil at 300° C at  $8 \times 10^{-5}$  Torr pressure and to be completely evaporated by 460° C. The mass spectra over this range were unchanged.

The triaryl phosphate fluid was found to have four main components in the gas chromatogram. In the mass spectrometer, a low boiling component comes off at 200° C at  $8 \times 10^{-5}$  Torr pressure. The structure of this compound is most likely:



with a parent molecular ion at 226 molecular weight and a base peak at 209 (phenol). At higher temperatures (300° C), other components whose spectra are consistent with partial phosphate esters of the same phenol, boiled off. It is likely that the four GC peaks observed were the phenol, a mono-ester, di-ester, and the tri-ester of phosphoric acid.

The petroleum base hydrocarbon fluid was also found to be a complex mixture of compounds. It began to boil at 250° C at  $8 \times 10^{-5}$  Torr pressure and continue boiling through 460° C. The mass spectra remain unchanged and exhibited the characteristics of long, branched chain hydrocarbons.

#### Incipient Boiling Point Determinations

The incipient boiling points (first bubble formation) were measured to  $\pm 2^\circ$  C at atmospheric pressure, with the following results:

<u>Hydraulic Fluid</u>	<u>Incipient Boiling Point</u>
Neopentyl polyol ester fluid	360° C
Petroleum base hydrocarbons fluid	350° C
Triaryl phosphate fluid	380° C

In each instance some discoloration was noted. The first two fluids turned "brown", the third "slightly brown". In addition, a black precipitate was formed in the triaryl phosphate fluid. All these observations imply a degree of thermal instability and probably pyrolytic decomposition in the vicinity of their atmospheric boiling points.

#### Chromatograms of Fluids Dissolved in CS<sub>2</sub>

Gas chromatography of the materials dissolved in carbon disulfide gave the chromatograms shown in Figures 2, 3, and 4 for neopentyl polyol ester, triaryl phosphate, and petroleum base hydrocarbons, respectively. The six main peaks in the neopentyl polyol ester probably represent polymeric esters of 1,3-dihydroxyneopentane. The four major peaks in the triaryl phosphate are probably the phenol, mono-, di-, and tri-esters of phosphoric acid. The petroleum base hydrocarbons gas chromatogram is typical of a complex hydrocarbon mixture.

#### OUTGASSING STUDIES

Both the raw data from the outgassing experiments and calculated results are shown in Tables 1, 2, and 3 for each of the three hydraulic fluids. The raw data are the quantities of CO, total hydrocarbons, NO<sub>x</sub>, total aldehydes, and in the case of triaryl phosphate fluids, total phosphorus. Since the raw data are based on the weight of the sample used, they have been converted to a common basis of 1 kg of material and also to a concentration (ppm) based on quantities outgassed from 1 kg in an average 28.38 m<sup>3</sup> (1000 ft<sup>3</sup>) space. Although spaces aboard Navy ships and submarines vary greatly in size, this volume is considered a representative median value. Threshold Limit Values (TLV), which are unofficial maximum concentrations of airborne contaminants, are included in Tables 1-3 as a base-line reference. TLV's listed are for an 8-hour time-weighted average exposure. Shipboard duty stations vary from 4 to 8 hours duration.

Also, no allowance is made for dilution of contaminants by shipboard ventilation. Thus, comparisons with TLV's must be considered only as rough guides.

hydraulic fluid. It is seen that, starting at 250° C, neopentyl polyol ester produced large amounts of carbon monoxide which exceeded the TLV limits (50 ppm). The TLV was exceeded by a factor of 3 at 250° C, and by a factor of 9 at 450° C. Starting at 100° C, emission of total aldehydes slightly exceeded the TLV (2 ppm). At 250° C total aldehydes exceeded the TLV by a factor of 84 and at 450° C by a factor of 125 (249/2). No hydrocarbons or nitrogen oxides were detected at any of the exposure temperatures.

TABLE 1 - CONSTITUENTS OF VAPOR OUTGASSED FROM NEOPENTYL POLYOL ESTER HYDRAULIC FLUID (0.0460 Gram-Sample)

Measured Constituent	Quantity Emitted by Sample (µg)				Cumulative Total Emitted g/kg	Resultant* Concentration ppm/kg (°C)	TLV** (ppm)
	(°C)						
	50	100	250	450			
Carbon Monoxide***	N11	N11	226	718	20.52	151(250)   Total 480(450)   631	50
Total Hydrocarbons	N11	N11	N11	N11	N11	N11	****
Nitrogen Oxides (as Nitrogen Dioxide)	N11	N11	N11	N11	N11	N11	5
Total Aldehydes (As Formal- dehyde)***	N11	3	270	296	14.54	249(450) } 168(250) } Total 2(100) } 419	2

3

\*In an average 28.38 m<sup>3</sup> space.

\*\*Threshold limit value for 8-hour time-weighted average exposure.<sup>8</sup>

\*\*\*Nuclear Powered Submarine Atmosphere Control Manual S9510-AB-ATM-010/  
SUB ATM Cont. gives the following limits in ppm:

	<u>90-day</u>	<u>24-hour</u>	<u>1-hour Emergency</u>
CO	15	200	200
HCHO	0.5	1	3

\*\*\*\*Threshold limit values are not assigned to mixtures.



Table 2 shows the results of outgassing the triaryl phosphate fluid. Between 100° and 450° C it produced carbon monoxide only slightly above the TLV. Between 250° and 450° C nitrogen oxides and total aldehydes exceeded TLV by factors of 2 and 6, respectively. No hydrocarbons or phosphorus were detected.

TABLE 2 - CONSTITUENTS OF VAPOR OUTGASSED FROM TRIARYL PHOSPHATE HYDRAULIC FLUID (0.0540 Gram-Sample)

Measured Constituent	Quantity Emitted by Sample (µg)				Cumulative Total Emitted g/kg	Resultant* Concentration ppm/kg (°C)	TLV** (ppm)
	°C						
	50	100	250	450			
Carbon Monoxide	N11	10	9	94	2.09	6(100) 5(200) 53(450) } Total 64	50
Total*** Hydrocarbons	N11	N11	N11	N11	N11	N11	****
Total Aldehydes (As Formal- dehyde) ***	N11	N11	5	17	0.41	9(100) 3(250) } Total 12	2
Total Phosphorus (As Phosphine)	N11	N11	N11	N11	N11	N11	0.3
Nitrogen Oxides (as Nitrogen Dioxide)	N11	N11	20	8	0.52	7(250) 3(450) } Total 10	5

\*In an average 28.38 m<sup>3</sup> space.

\*\*Threshold limit value for 8-hour time-weighted average exposure.<sup>8</sup>

\*\*\*Nuclear Powered Submarine Atmosphere Control Manual S9510-AB-ATM-010/  
SUB ATM Cont. gives the following limits in ppm:

	<u>90-day</u>	<u>24-hour</u>	<u>1-hour Emergency</u>
CO	15	200	200
HCHO	0.5	1	3

\*\*\*\*Threshold limit values are not assigned to mixtures.

Table 3 shows the results of outgassing the petroleum base hydrocarbons hydraulic fluid. At 250° C carbon monoxide levels did not exceed the TLV (50 ppm). At 450° C the amount of carbon monoxide produced was slightly above the TLV. Emission of total aldehydes occurred only at 450° C but exceeded the TLV (2 ppm) by a factor of 13. No hydrocarbons or nitrogen oxides were detected.

**TABLE 3 - CONSTITUENTS OF VAPOR OUTGASSED FROM PETROLEUM  
BASE HYDROCARBONS HYDRAULIC FLUID (0.0458 Gram-Sample)**

Measured Constituent	Quantity Emitted by Sample (μg)				Cumulative Total Emitted g/kg	Resultant* Concentration ppm/kg (°C)	TLV** (ppm)
	°C						
	50	100	250	450			
Carbon Monoxide	N11	N11	72	76	3.23	51(450) Total 48(250) 99	50
Total*** Hydrocarbons	N11	N11	N11	N11	N11	N11	****
Nitrogen Oxides (as Nitrogen Dioxide)	N11	N11	N11	N11	N11	N11	5
Total Aldehydes (As Formal- dehyde)***	N11	N11	N11	40	0.92	26	2

\*In an average 28.38 m<sup>3</sup> space.

\*\*Threshold limit value for 8-hour time-weighted average exposure.<sup>8</sup>

\*\*\*Nuclear Powered Submarine Atmosphere Control Manual S9510-AB-ATM-010/  
SUB ATM Cont. gives the following limits in ppm:

	<u>90-day</u>	<u>24-hour</u>	<u>1-hour Emergency</u>
CO	15	200	200
HCHO	0.5	1	3

\*\*\*\*Threshold limit values are not assigned to mixtures.

All three tables reveal an absence of outgassed material at 50° C and only 10 μg of CO from the triaryl phosphate and 3 μg of aldehydes from the neopentyl polyol ester at 100° C. Starting at 100° C, sample vapors would rise and condense on the glass walls of the heat exposure chamber immediately around the platinum boat. This condensate would not transfer toward the collecting system even under the strong stream of circulating air. It is presumed that a low vapor pressure and a high molecular weight explains this phenomena and why no outgassed constituents were detected at 50° and 100° C exposures. One may further interpret this resistance of vapors to transfer as a low tendency of such vapors to contaminate a given space if the temperature does not exceed 100° C.

### CONCLUSIONS

Based on the single samples studied:

1. The neopentyl polyol ester hydraulic fluid was found to emit CO and aldehydes in quantities which would greatly exceed the TLV if 1 kg of the fluid were heated to a temperature of 250° C in a 28.38 m<sup>3</sup> space.
2. The triaryl phosphate hydraulic fluid was found to emit CO, NO<sub>x</sub>, and aldehydes. These emissions would slightly exceed the corresponding TLV's in a 28.38 m<sup>3</sup> space if a 1 kg quantity of the fluid were heated to 450° C. No phosphorus emissions were detected, but a large amount of a phenol type constituent was identified in the fluid by GC/MS techniques.
3. The petroleum base hydrocarbons hydraulic fluid was found to emit CO at a temperature of 250° C and aldehydes at a temperature of 450° C. These emissions at 450° C would exceed the corresponding TLV's if a 1 kg quantity of the fluid was heated at these temperatures in the standard 28.38 m<sup>3</sup> space.

### RECOMMENDATION

It is recommended that further outgassing studies be carried out on additional samples of each of the classes of hydraulic fluids studied to establish whether or not the behavior observed in this study is typical since the chemical character and toxic properties of these materials are not included in the military specifications and, therefore, are not checked. This will provide a basis for materials modifications/substitutions to reduce potential hazards.

- T = Thermocouple
- S = Platinum Boat for Sample
- J = Sampling Port
- I<sub>1</sub>, I<sub>2</sub> = Impingers with Scrubbing Solutions
- D = Drying Tube (CaCl<sub>2</sub>)
- C<sub>1</sub>, C<sub>2</sub> = Charcoal Tubes
- F = Flowmeter
- E = Circulating Air Pump
- W = Removable Swagelock Fitting
- P = Pyrolysis Chamber
- H = Heat Coil

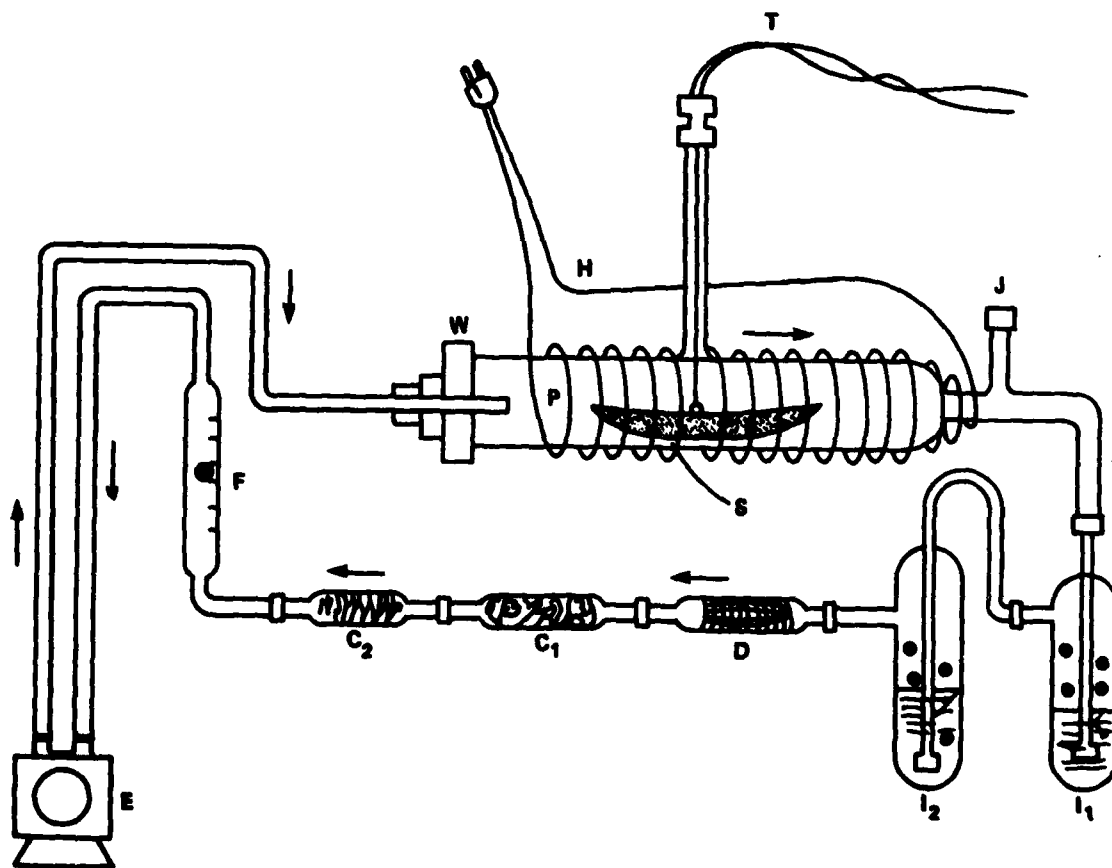


Figure 1 - Apparatus for Heat Exposure and Collection of Outgassed Products of Hydraulic Fluids

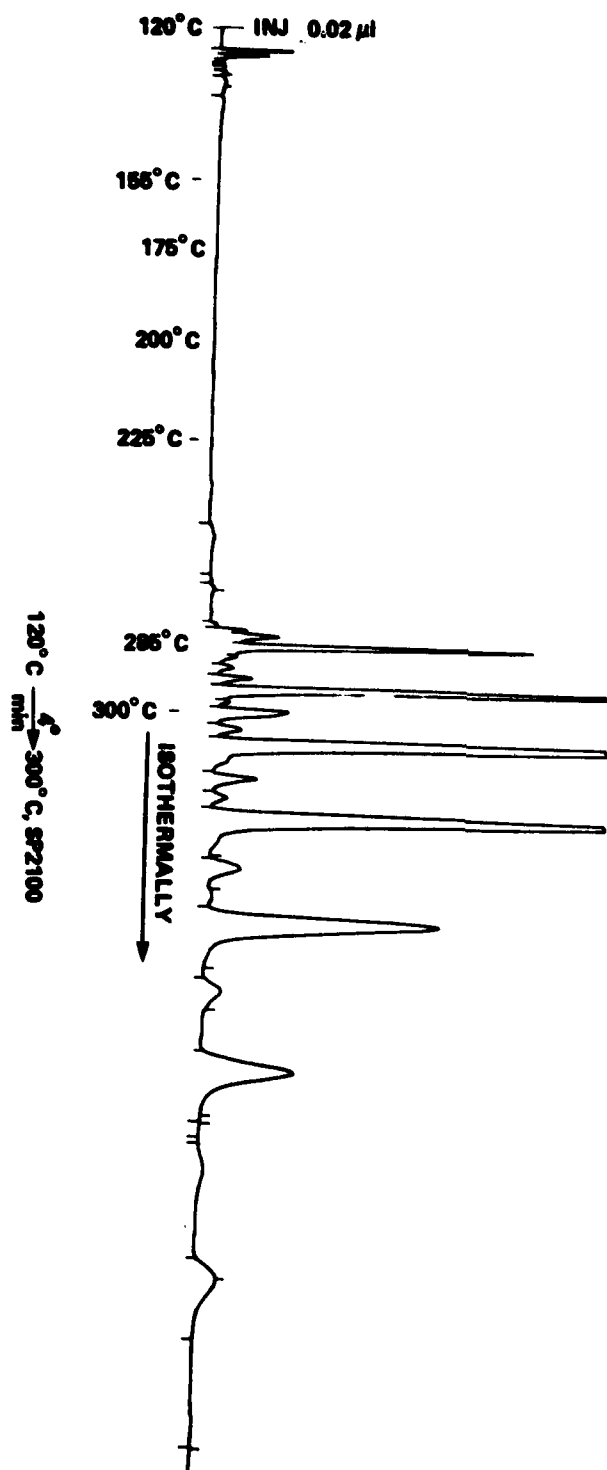


Figure 2 - Gas Chromatogram of Neopentyl Polyol Ester

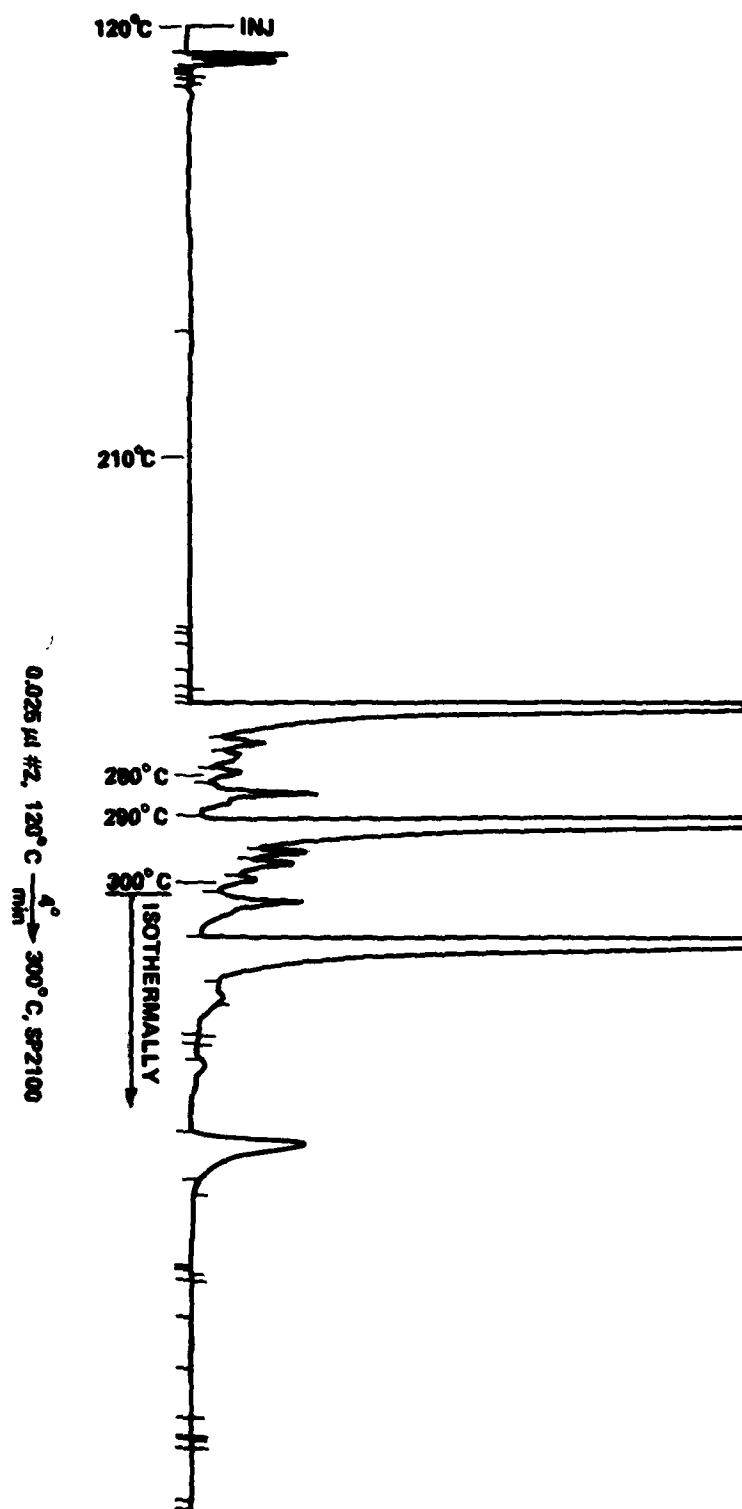


Figure 3 - Gas Chromatogram of Triaryl Phosphate

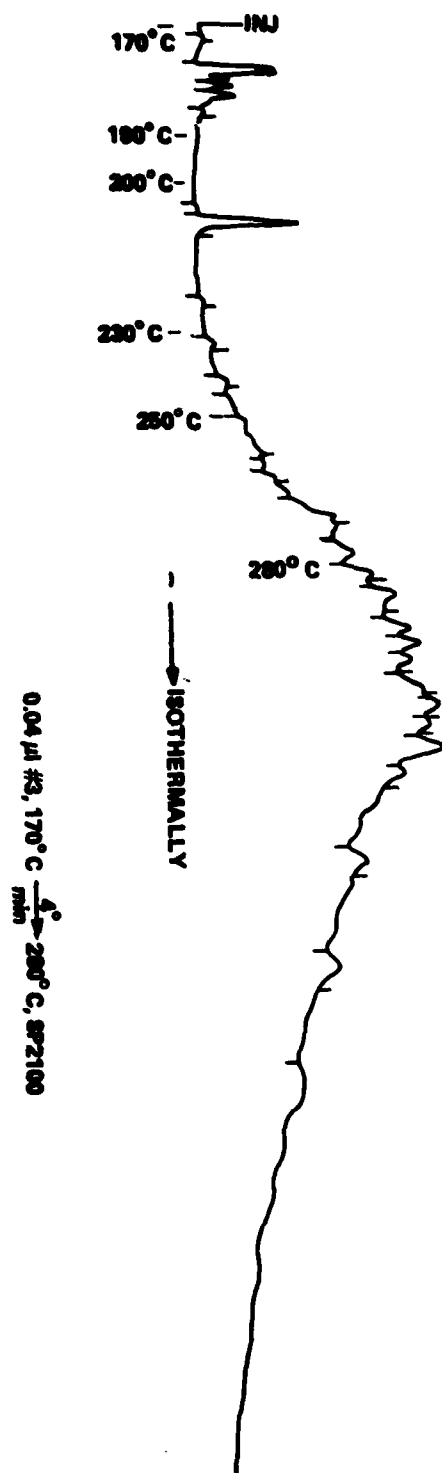


Figure 4 - Gas Chromatogram of Petroleum Base Hydrocarbons

## APPENDIX

### METHOD FOR PHOSPHINE DETERMINATION

1. Place 4 ml of absorbing solution from impinger in a small beaker.
2. Add 1 ml of 0.12N  $\text{AgNO}_3$  into the beaker followed by 0.25 ml of concentrated HCl.
3. Warm beaker slightly and filter into a test tube through Whatman No. 12 filter paper.
4. Add 0.25 ml of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  solution (25 g/l) and shake.
5. Add 1 drop of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  solution (25 g/l) in 1 liter of glycerine and shake.
6. Read absorbance at 650 nanometers. (A Bausch and Lomb Spectronic 20 instrument may be used.) Determine phosphate ( $\text{PO}_4^{3-}$ ) concentration from a calibration curve obtained as described in ASTM method D515-68.
7. Multiply the  $\text{PO}_4^{3-}$  concentration by 0.358 to obtain equivalent  $\text{PH}_3$  concentration.



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Also, no allowance is made for dilution of contaminants by shipboard ventilation. Thus, comparisons with TLV's must be considered only as rough guides. Table 1 shows the results of outgassing the neopentyl polyol ester hydraulic fluid. It is seen that, starting at 250° C, neopentyl polyol ester produced large amounts of carbon monoxide which exceeded the TLV limits (50 ppm). The TLV was exceeded by a factor of 3 at 250° C, and by a factor of 9 at 450° C. Starting at 100° C, emission of total aldehydes slightly exceeded the TLV (2 ppm). At 250° C total aldehydes exceeded the TLV by a factor of 84 and at 450° C by a factor of 125 (249/2). No hydrocarbons or nitrogen oxides were detected at any of the exposure temperatures.

TABLE 1 - CONSTITUENTS OF VAPOR OUTGASSED FROM NEOPENTYL POLYOL ESTER HYDRAULIC FLUID (0.0460 Gram-Sample)

Measured Constituent	Quantity Emitted by Sample (µg)				Cumulative Total Emitted g/kg	Resultant* Concentration		TLV** (ppm)
	(°C)					ppm/kg (°C)		
	50	100	250	450				
Carbon Monoxide***	N11	N11	226	718	20.52	151(250)   Total 480(450)   631	50	
Total Hydrocarbons	N11	N11	N11	N11	N11	N11	****	
Nitrogen Oxides (as Nitrogen Dioxide)	N11	N11	N11	N11	N11	N11	5	
Total Aldehydes (As Formal- dehyde)***	N11	3	270	296	14.54	249(450) } 168(250) } Total 2(100) } 419	2	

\*In an average 28.38 m<sup>3</sup> space.

\*\*Threshold limit value for 8-hour time-weighted average exposure.<sup>8</sup>

\*\*\*Nuclear Powered Submarine Atmosphere Control Manual S9510-AB-ATM-010/  
SUB ATM Cont. gives the following limits in ppm:

	<u>90-day</u>	<u>24-hour</u>	<u>1-hour Emergency</u>
CO	15	200	200
HCHO	0.5	1	3

\*\*\*\*Threshold limit values are not assigned to mixtures.

Table 2 shows the results of outgassing the triaryl phosphate fluid. Between 100° and 450° C it produced carbon monoxide only slightly above the TLV. Between 250° and 450° C nitrogen oxides and total aldehydes exceeded TLV by factors of 2 and 6, respectively. No hydrocarbons or phosphorus were detected.

TABLE 2 - CONSTITUENTS OF VAPOR OUTGASSED FROM TRIARYL PHOSPHATE HYDRAULIC FLUID (0.0540 Gram-Sample)

Measured Constituent	Quantity Emitted by Sample (μg)				Cumulative Total Emitted g/kg	Resultant* Concentration ppm/kg (°C)	TLV** (ppm)
	°C						
	50	100	250	450			
Carbon Monoxide	N11	10	9	94	2.09	6(100) 5(200) 53(450) } Total 64	50
Total*** Hydrocarbons	N11	N11	N11	N11	N11	N11	****
Total Aldehydes (As Formaldehyde) ***	N11	N11	5	17	0.41	9(100) 3(250) } Total 12	2
Total Phosphorus (As Phosphine)	N11	N11	N11	N11	N11	N11	0.3
Nitrogen Oxides (as Nitrogen Dioxide)	N11	N11	20	8	0.52	7(250) 3(450) } Total 10	5

\*In an average 28.38 m<sup>3</sup> space.

\*\*Threshold limit value for 8-hour time-weighted average exposure.<sup>8</sup>

\*\*\*Nuclear Powered Submarine Atmosphere Control Manual S9510-AB-ATM-010/ SUB ATM Cont. gives the following limits in ppm:

	90-day	24-hour	1-hour Emergency
CO	15	200	200
HCHO	0.5	1	3

\*\*\*\*Threshold limit values are not assigned to mixtures.

Table 3 shows the results of outgassing the petroleum base hydrocarbons hydraulic fluid. At 250° C carbon monoxide levels did not exceed the TLV (50 ppm). At 450° C the amount of carbon monoxide produced was slightly above the TLV. Emission of total aldehydes occurred only at 450° C but exceeded the TLV (2 ppm) by a factor of 13. No hydrocarbons or nitrogen oxides were detected.